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Structure-Property Relationships for Polycyanurate Networks Derived from Renewable Sources

18 August 2015

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Outline

- Background
- Experimental Setup
  - Monomer Structure Modifications
  - Physical Property Data
  - Explanation of Structural Parameters
- Results and Conclussions
  - Partial Least-Squares Regression results
  - Measured and Predicted values of selected monomer properties

Acknowledgements: Air Force Office of Scientific Research, Air Force Research Laboratory – Program Support; PWG team members (AFRL/RQRP)

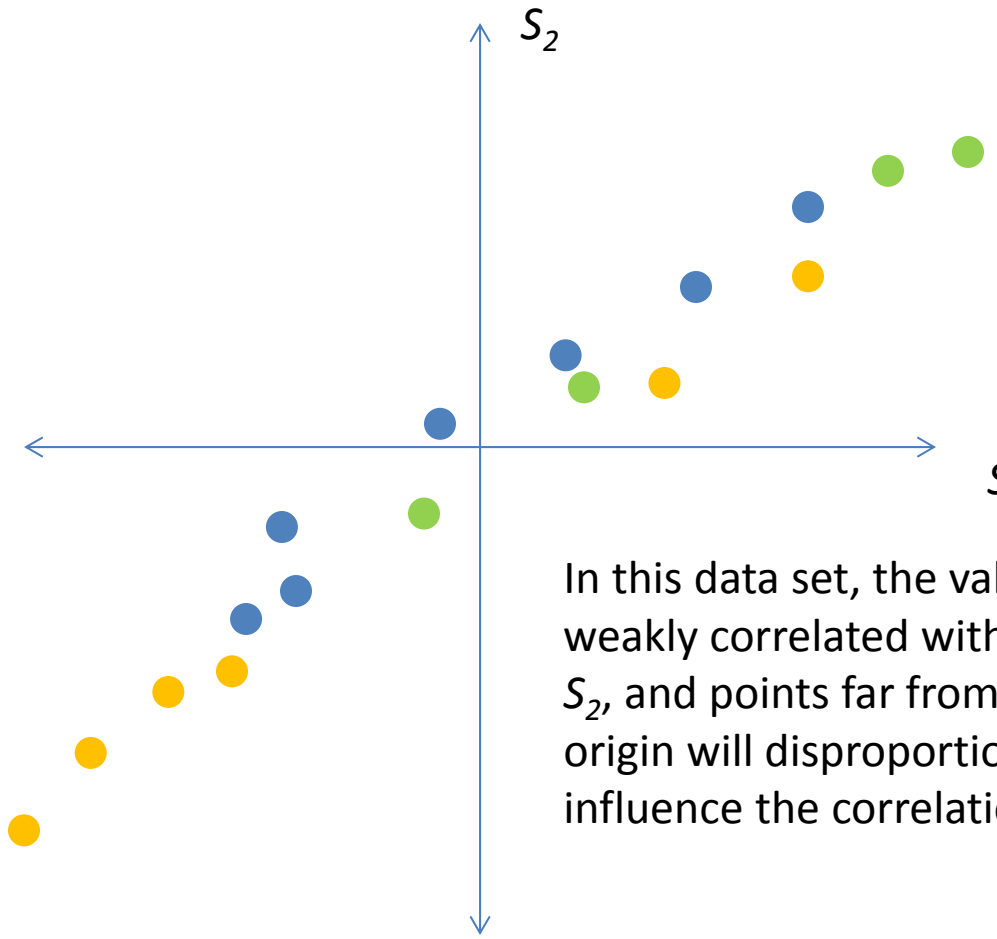
Background

- The recent synthesis of a wide variety of cyanate ester monomers that may be derived from renewable resources has created a newly available set of chemical structures that, due to a wide range of chemical features, provide a unique opportunity for the development of quantitative structure-property relationships for dicyanate esters and their polymerized networks.
- Specific structure-property relationships for monomer melting point, glass transition temperature at full conversion, and char yields at 600 °C under nitrogen and air have been developed with the aid of partial least squares methods.
- The predictions inherent in these structure-property relationships are examined and compared to predictions based on ordinary least squares methods.
- Specific predictions for the properties of two as-yet unsynthesized dicyanate ester monomers derived from renewable resources are also presented.

Materials and Methods

- **Materials and Data Sources**
  - –The 19 monomers / networks chosen for analysis contain only the elements C, H, N, and O.
  - –All feature two aromatic rings containing one or more cyanate ester / cyanurate linkages, connected by a bridge containing only non-aromatic hydrocarbons.
  - –Two of the monomers are derived from petroleum; they are the well-known Primaset BADCy and Primaset LECy (dicyanate esters of bisphenol A and E, respectively).
  - –17 have been derived from a variety of plant compounds. The networks chosen for comparison have all been analyzed using either identical or nearly identical protocols in our laboratories, thereby helping to ensure that comparisons reflect meaningful differences.
- **Methods of Analysis**
  - – Partial Least Squares and Least Squares regressions run and compared
  - – Consistent scheme of non-duplicative parameters established
  - – Minimum of ten parameters needed to describe a single monomer
  - – Five parameters describing the substitution pattern around the ring, valued between 0 and 1
  - – Five parameters describing the bridge structure, valued any number above 0.
  - – PLS regressions were carried out using the SIMPLS algorithm in MATLAB, which centers the data, but does not require normalization

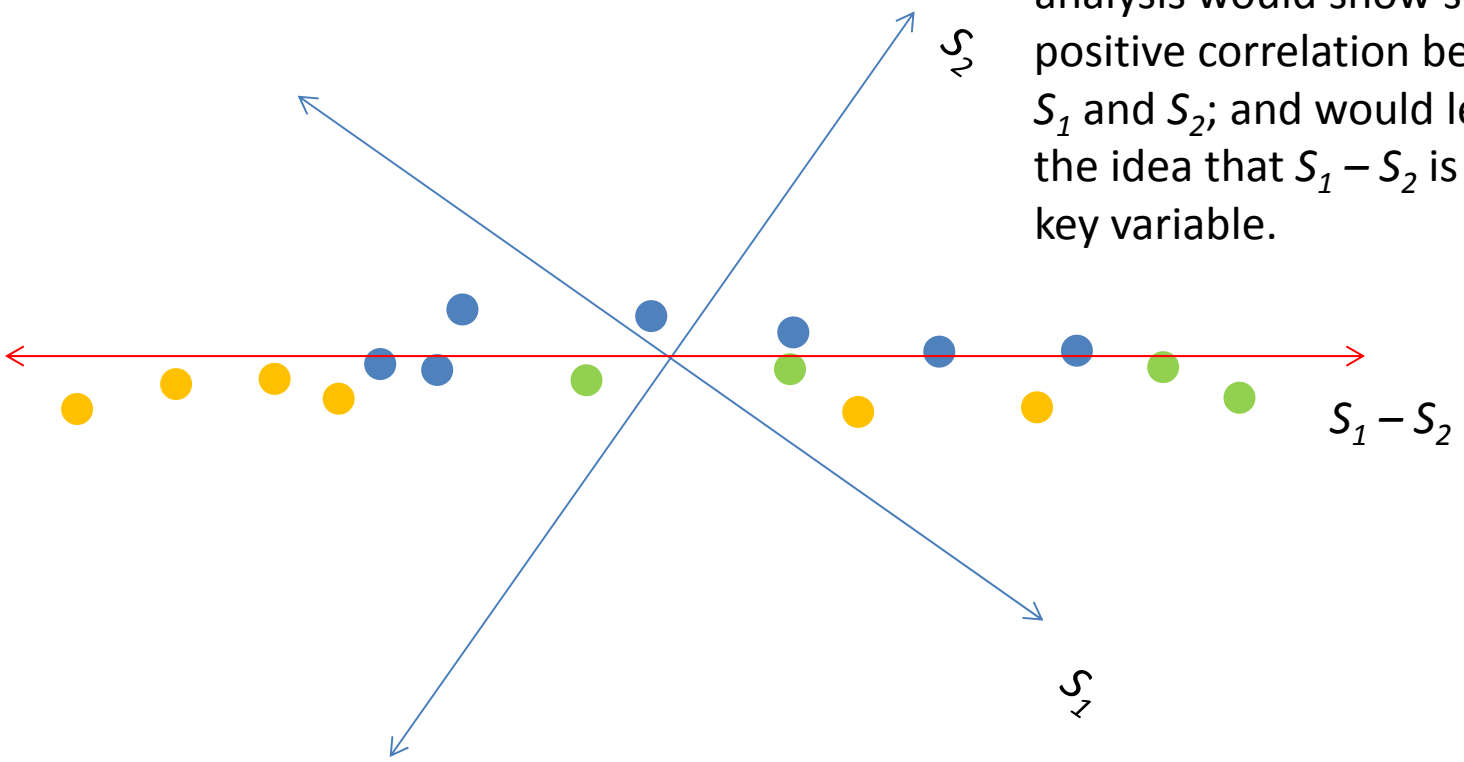
Example: Latent Variables, PCA, and PLS



In this data set, the value of *P* is weakly correlated with S_1 and S_2, and points far from the origin will disproportionately influence the correlation

P values: blue = below average; green = about average; orange = above average

Example: Latent Variables, PCA, and PLS



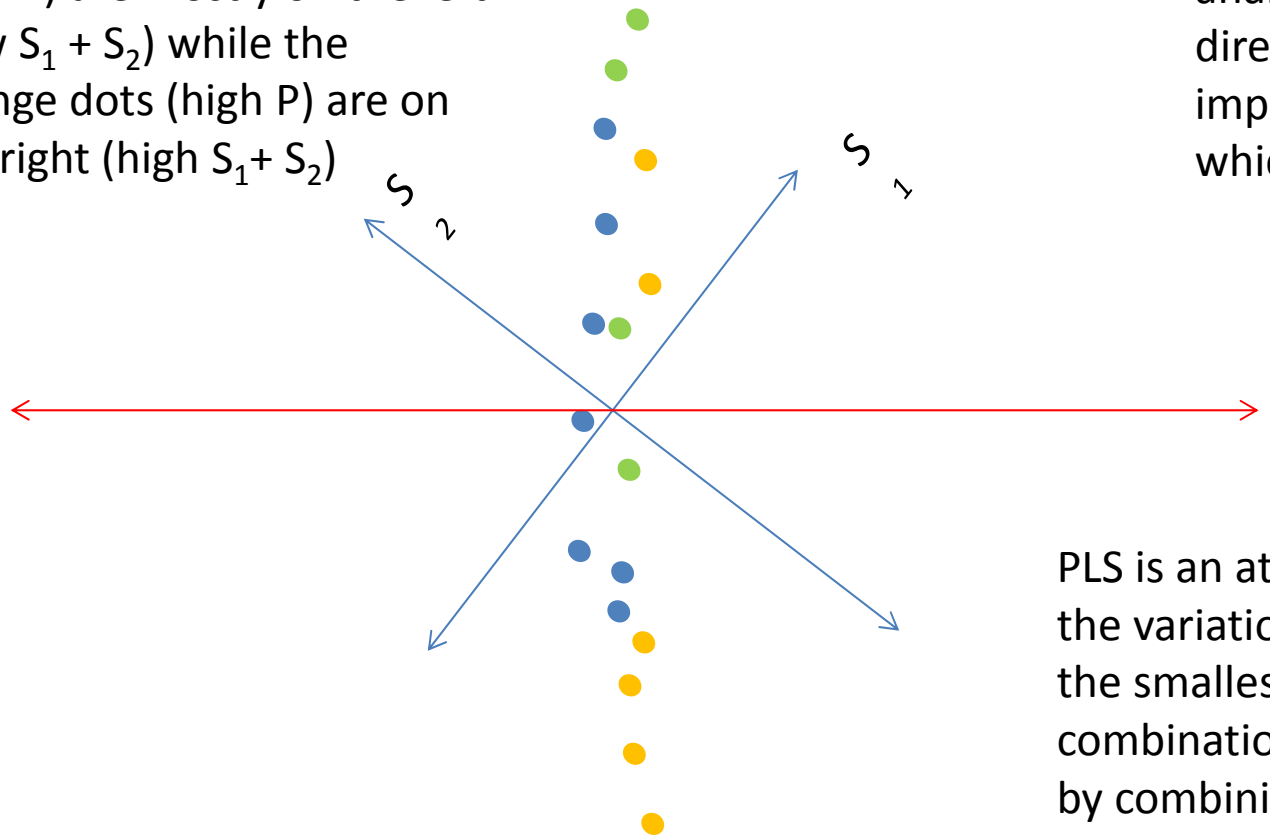
A principal components analysis would show strong positive correlation between S_1 and S_2; and would lead to the idea that $S_1 - S_2$ is the key variable.

P values: blue = below average; green = about average; orange = above average

Example: Latent Variables, PCA, and PLS

Notice that the blue dots (low P) are mostly on the left (low $S_1 + S_2$) while the orange dots (high P) are on the right (high $S_1 + S_2$)

A reduced rank regression analysis would consider the direction having the greatest impact on the value of *P*, which is actually $S_1 + S_2$



PLS is an attempt to describe the variation in P in terms of the smallest number of combinations of factors of S by combining PCR and RRR

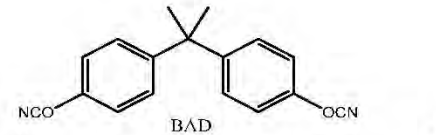
P values: blue = below average; green = about average; orange = above average

Cross-Validation

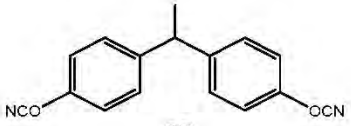
- Cross-validation is used to estimate the error in predicting the properties of an entirely new structure based on a model developed by any regression technique (including PLS).

- To perform cross-validation, the data set is divided into two parts, a “training set” (usually 90% of data) and a “test set” (10% of data). Regression is performed with the training set to develop a cross-validation model, then the model is used to predict the values in the test set. The process may be repeated with many different training and test sets. The prediction is characterized by the mean square error of predictions.

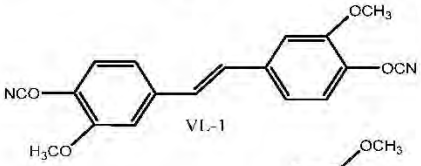
Structures of Monomers



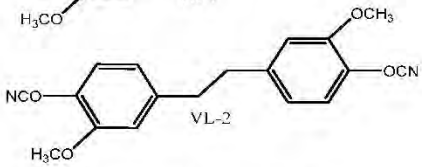
BAD



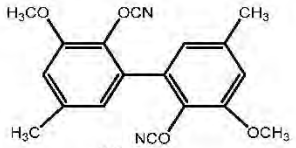
LE



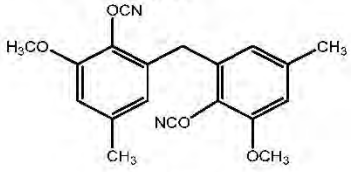
VL-1



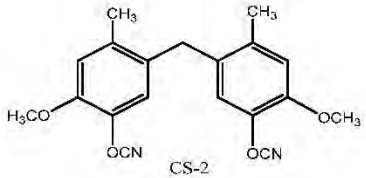
VL-2



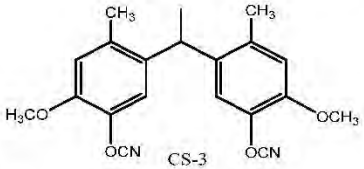
VL-3



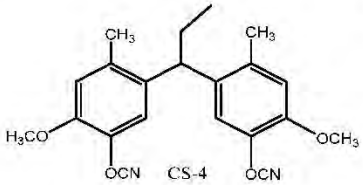
CS-1



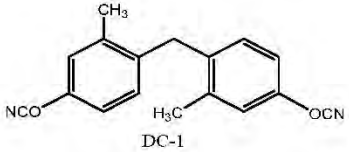
CS-2



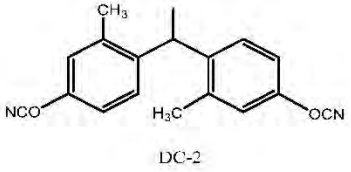
CS-3



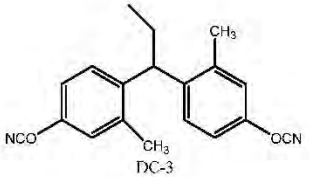
CS-4



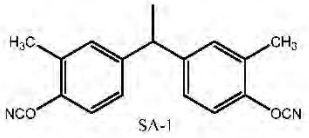
DC-1



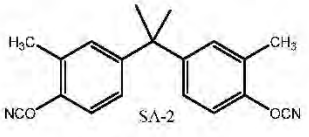
DC-2



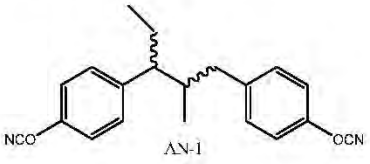
DC-3



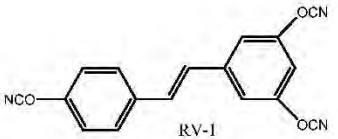
SA-1



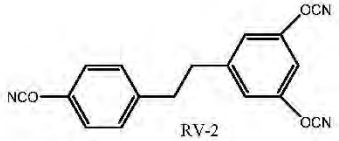
SA-2



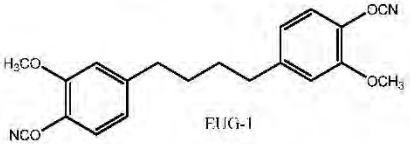
AN-1



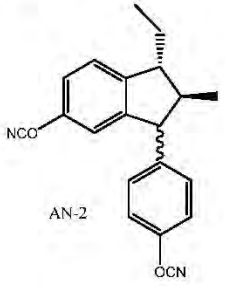
RV-1



RV-2

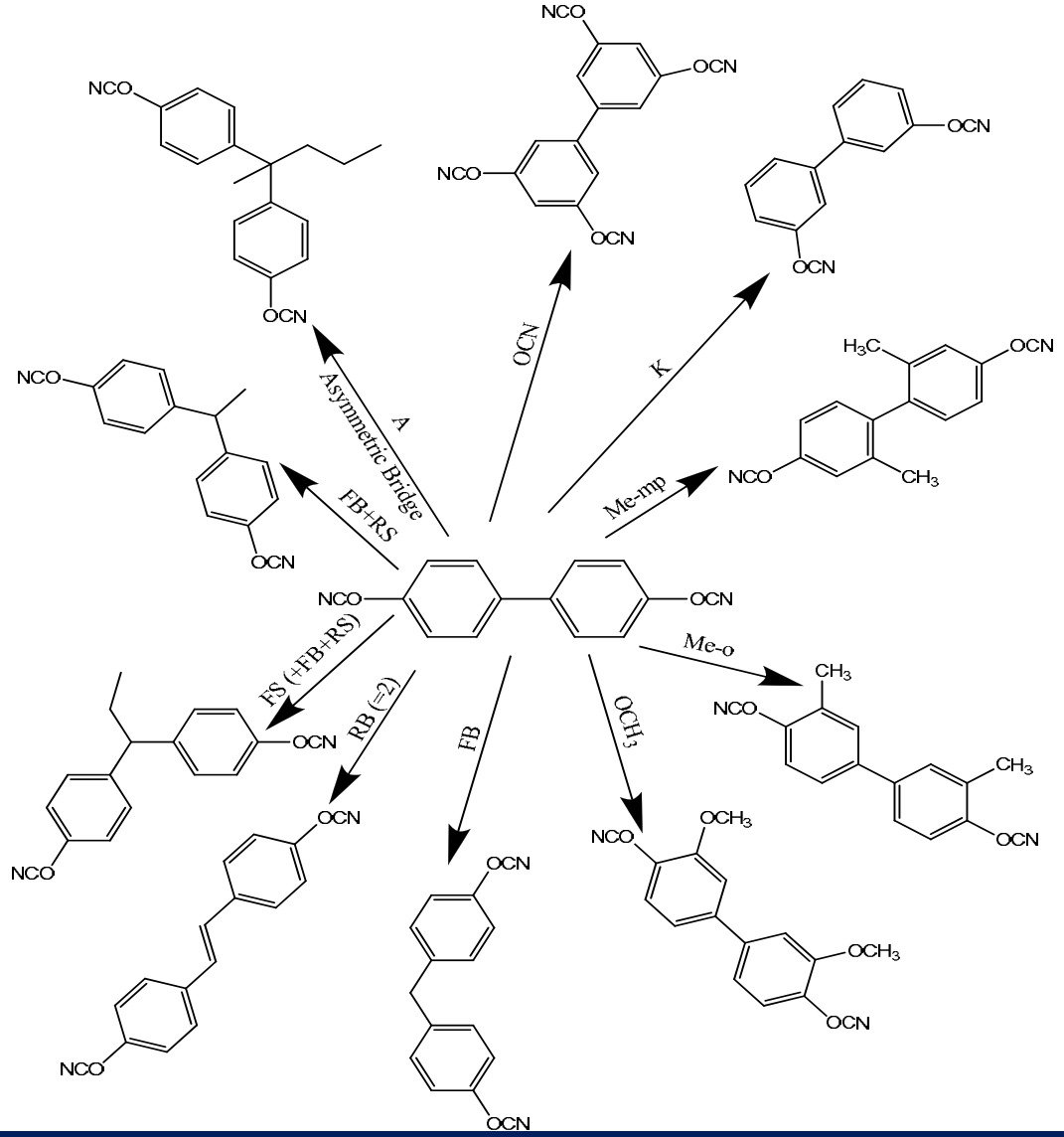


EUG-1



AN-2

Structural Parameter Illustration



Physical property data used in structure-property correlation

Monomer/network	T_m (°C)[a]	$T_{G\text{-}fc}$ (°C)[b]	Char Yield (N_2, %)	Char Yield (Air, %)	Source
BAD	83	323	47	25	9
LE	Liquid[c]	295	54	24	9
AN-1	Liquid[c]	223	31	9	9
AN-2	72	313	48	6	9
CS-1	151	236	33	8	10
CS-2	125	240	35	11	10
CS-3	98	206	28	11	10
CS-4	120	238	27	11	10
DC-1	88	259	53	30	11[d]
DC-2	105	283	43	4	11[d]
DC-3	Liquid[c]	273	43	3	11[d]
EUG-1	104	167	31	1	12
RV-1	156	>340	74	71	13
RV-2	123	334	70	66	13
SA-1	73	236	48	11	14
SA-2	82	237	43	8	14
VL-1	237	n/a	n/a	n/a	15
VL-2	190	n/a	n/a	n/a	15
VL-3	205	n/a	n/a	n/a	15

Explanation of Structural Parameters

Parameter	Explanation
OCN	Additional -OCN groups per monomer (e.g. 1 for tricyanates)
K	"Kinked" -OCN groups (that is, -OCN groups -ortho or -meta to bridge junction); 1 if any such groups are present on a cyanated aromatic ring; 0 if not present on a cyanated ring; averaged over all cyanated aromatic rings in monomer (e.g. 0 for the typical 4,4' – OCN substitution pattern in dicyanate monomers)
Me-mp	Methyl groups in positions -meta or -para to -OCN groups; 1 if any such groups are present on a single aromatic ring; 0 if not present; averaged over all cyanated aromatic rings in monomer
Me-o	Methyl groups in positions -ortho to -OCN groups; counting / averaging rules are the same as for Me-mp.
OCH_3	Methoxy groups on cyanated aromatic rings; counting / averaging rules are the same as for Me-mp
FB	"Flexible" non-hydrogen atoms in bridge "backbone" structure; the "backbone" of the bridge is defined as the set of non-hydrogen atoms bonded along the shortest possible path connecting two cyanated aromatic rings; if more than one such path exists, atoms in all such paths count, if more than one bridge exists, the total number of flexible non-hydrogen atoms in all bridge structures is counted, with each counted only once; "flexible" is defined as having sp^3 hybridization and being bonded to at least two other atoms (e.g. not a chain terminus) not in a ring; sp^3 atoms in ring structures considered on a case by case basis.

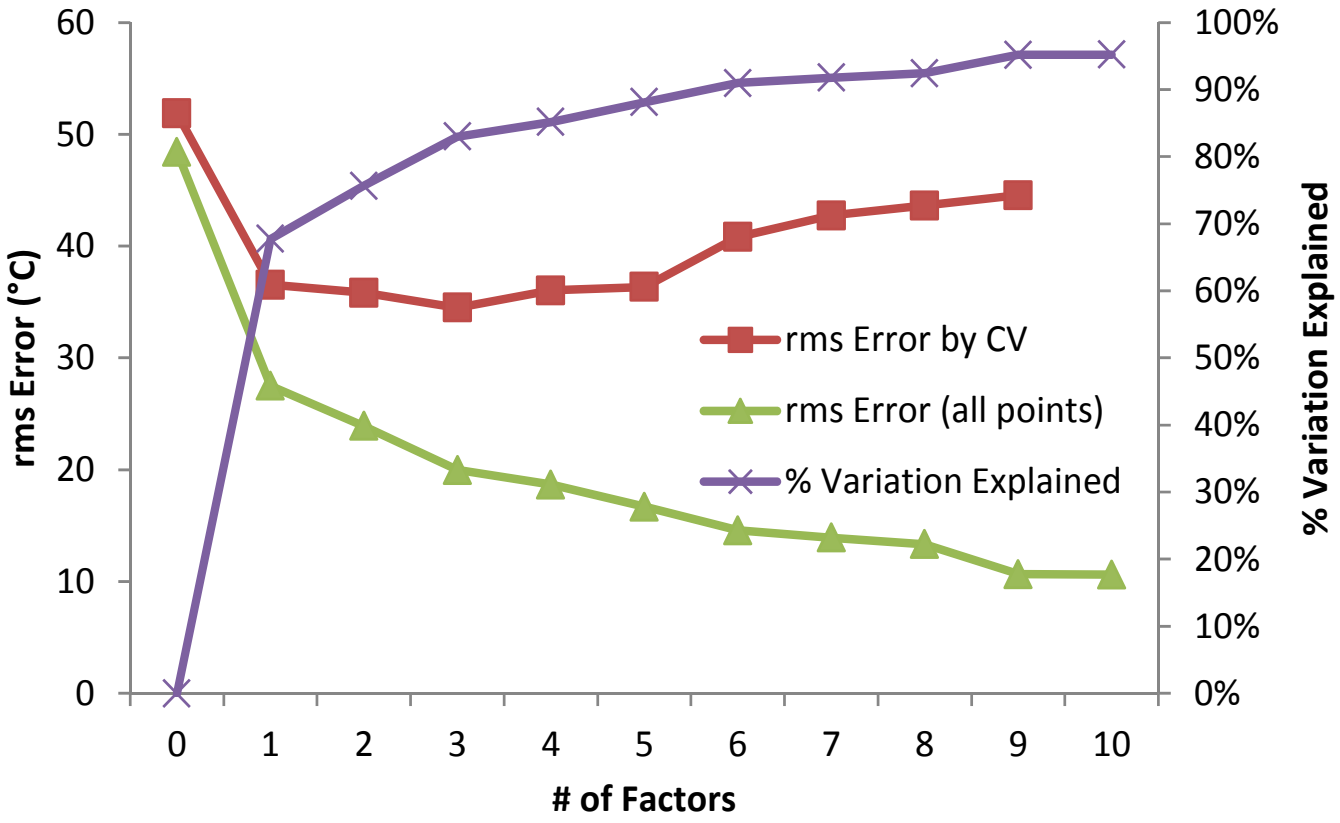
Explanation of Structural Parameters

Parameter	Explanation
RB	"Rigid" non-hydrogen atoms in bridge "backbone" structure. "Rigid" is defined as any non-hydrogen atom not meeting the criteria for "flexible", with sp^3 atoms in ring structures considered on a case by case basis. Non-hydrogen atoms that terminate chains, such as methyl carbons, and hydroxyl oxygens, count as "rigid". Rules for backbones and bridges are the same as for FB.
FS	"Flexible" non-hydrogen atoms in bridge "side group" structures. "Flexible" is defined as in FB, and the rules for counting paths and bridges are the same as in FB. A "side group" atom is any non-hydrogen atom in a structure bridging cyanated aromatic rings that is not counted as part of the "backbone"
RS	"Rigid" non-hydrogen atoms in "side group" bridge structures; definitions and rules are the same as for FB, RB, and FS (e.g. an isopropylidene bridge will have FB=1 and RS=2).
A	Asymmetric bridge. 1 if a bridge group is symmetrically substituted along its backbone(s), 0 if not, averaged over all bridge structures. Bridge and backbone are defined as in FB.

Structural parameter values for all monomers

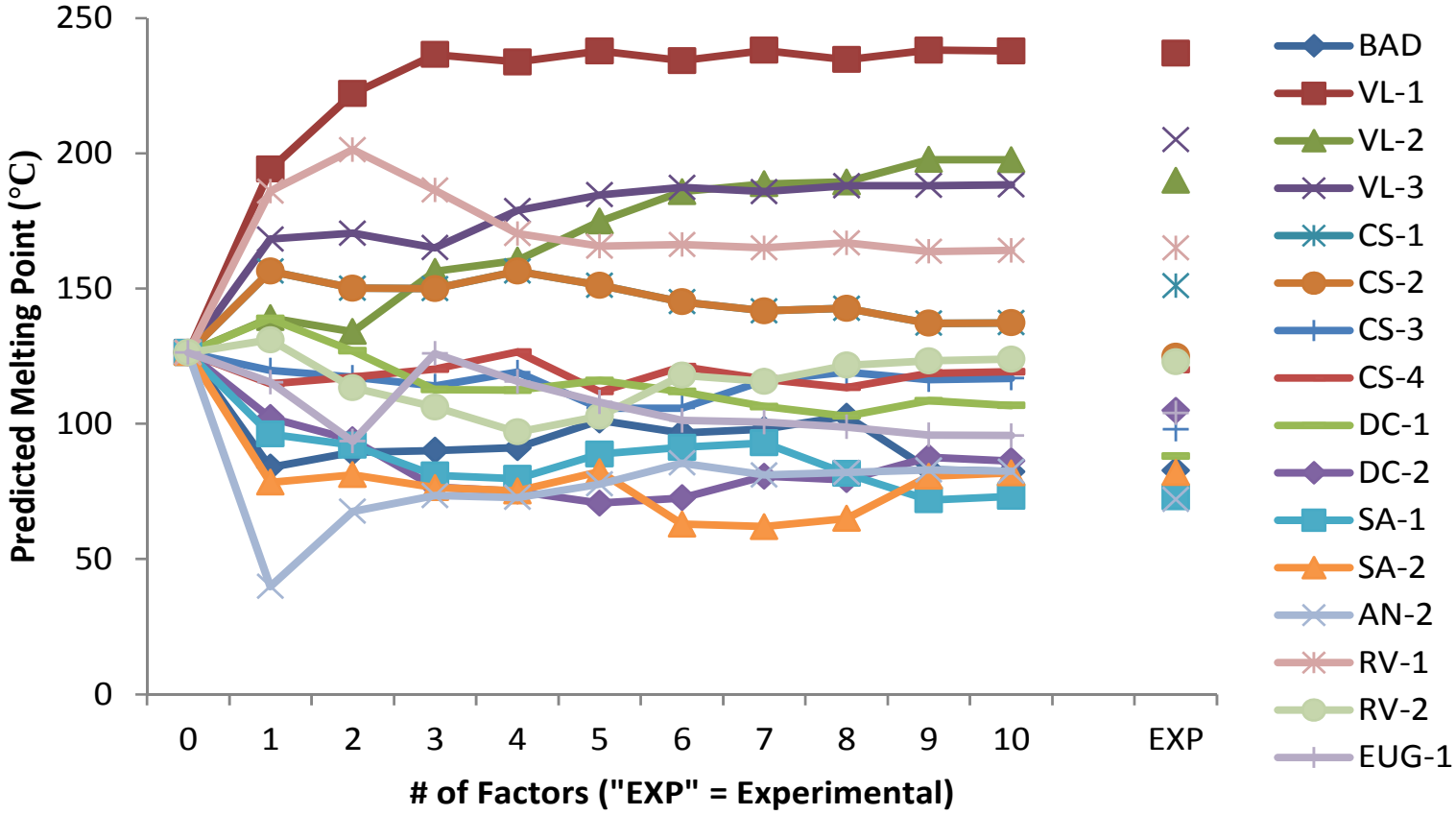
Mono-mer	OCN	K	Me-mp	Me-o	OCH3	FB	RB	FS	RS	A
BAD	0	0	0	0	0	1	0	0	2	0
LE	0	0	0	0	0	1	0	0	1	1
AN-1	0	0	0	0	0	3	0	1	2	1
AN-2	0	0	0	0	0	0.5	0.5	1.5	3.5	1
CS-1	0	1	1	0	1	1	0	0	0	0
CS-2	0	1	1	0	1	1	0	0	0	0
CS-3	0	1	1	0	1	1	0	0	1	1
CS-4	0	1	1	0	1	1	0	1	1	1
DC-1	0	0	1	0	0	1	0	0	0	0
DC-2	0	0	1	0	0	1	0	0	1	1
DC-3	0	0	1	0	0	1	0	1	1	1
EUG-1	0	0	0	0	1	4	0	0	0	0
RV-1	1	0.5	0	0	0	0	2	0	0	0
RV-2	1	0.5	0	0	0	2	0	0	0	0
SA-1	0	0	0	1	0	1	0	0	1	1
SA-2	0	0	0	1	0	1	0	0	2	0
VL-1	0	0	0	0	1	0	2	0	0	0
VL-2	0	0	0	0	1	2	0	0	0	0
VL-3	0	1	1	0	1	0	0	0	0	0
AN-U	0	0	0	0	0	1	2	1	2	1
EUG-U	0	0	0	0	1	2	0	0	0	0

Partial least squares regression characteristics as a function of the number of regression components present



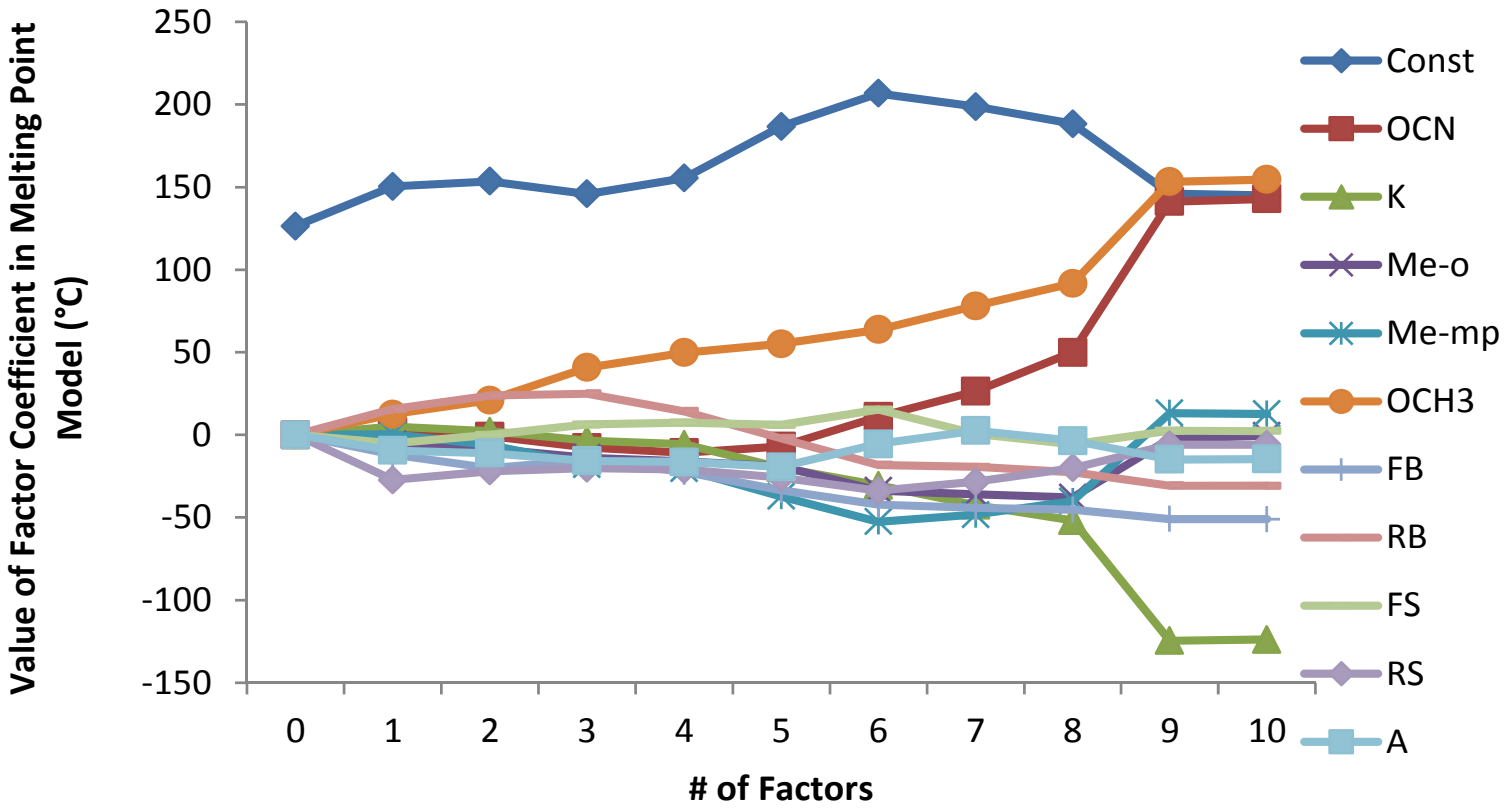
- Although the rms error associated with the regression itself decreases as more factors are added, “leave one out” cross-validation shows that the predictive error is minimized with only three factors

Predicted melting point values as a function of the number of partial least squares regression components.



- Tracking of individual predictions shows that, after about 4 factors are present, the role of additional factors is primarily to “fix” individual errors (such as VL-2). These “individual fixes” add no general predictive power, and likely degrade it

Melting point regression coefficients as a function of the number of partial least squares regression components.



- Although the predicted melting points do not change much, the coefficient values become unstable in about half the cases after the 3rd or 4th factor is added, indicating that the regression is being distorted more and more in order to custom-fit the specific data set. Such distortions destroy the general predictive power of the regression.

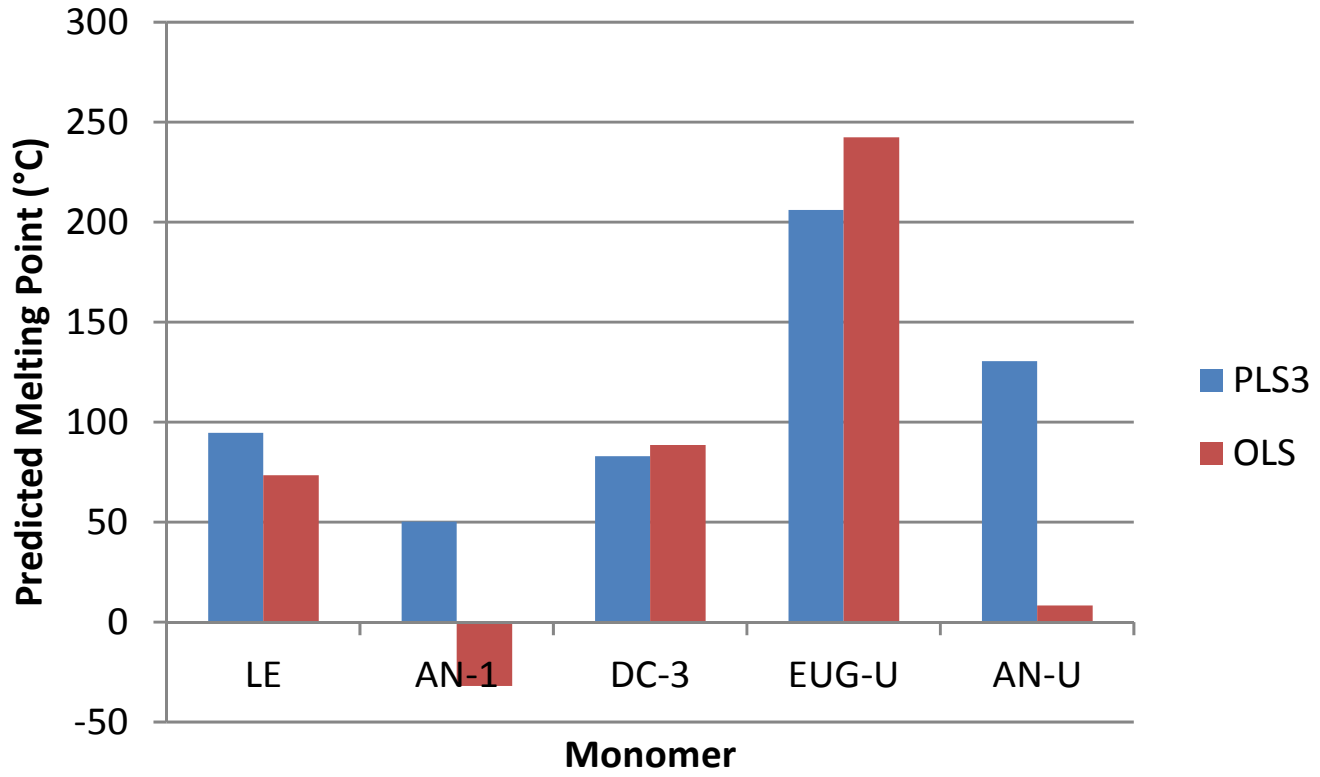
Linear regression model coefficients for melting point

Regression Types:
PLS = Partial Least Squares (3 factor)
OLS = Ordianry Least Squares

Factor	PLS	OLS
Constant	145.88	144.97
OCN	-7.64	142.86
K	-3.44	-123.97
Me-o	-13.73	-0.42
Me-mp	-18.07	12.73
OCH3	40.74	154.55
FB	-15.17	-50.97
RB	24.92	-30.87
FS	6.21	2.37
RS	-20.27	-5.86
A	-15.69	-14.60

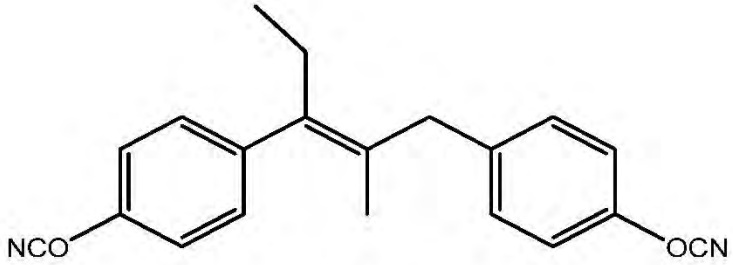
- Note how ordinary least squares multiple regression fits of the data set produce very large coefficients for the facotrs, which are not physically realistic for a linear model of melting points. In contrast, the coefficient values derived from partial least squares are reasonable.

Predicted melting points of monomers not included in regression models

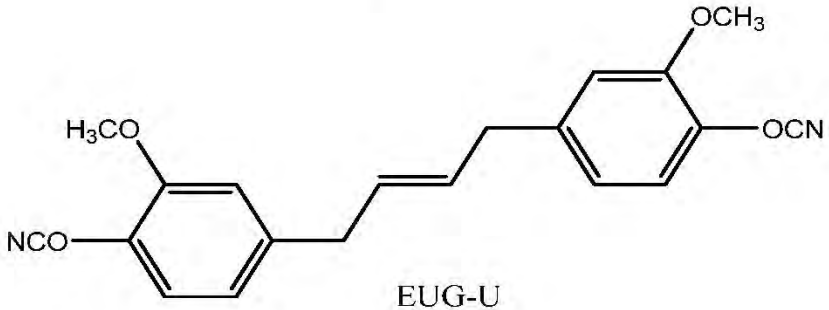


- Primaset® LECy ("LE") melts at 30 °C. "AN-1" is a liquid at room temperature (though it may be supercooled, so it could melt at up to 70 °C. "DC-3" is also a liquid at room temperature. "EUG-U" and "AN-U" have not been synthesized, but the partial least squares model predicts "AN-U" will be a high-melting solid, whereas ordinary least squares predicts it will be liquid at room temperature.

Chemical structures of the as-yet unsynthesized monomers AN-U and EUG-U.



AN-U



EUG-U

Summary

- Using a set of 19 cyanate ester monomers, 17 of which may be derived from renewable sources, structure property relationships, in the form of partial linear regression models, have been produced for the monomer melting point and compared to more traditional models based on ordinary least squares
- The partial least squares method was able to provide linear models based on a set of 10 structural parameters that predicted melting points to within about 35 °C,
- The predictive power of the patial least squares models was compared to that of ordinary least squares and shown to be at least as good.
- Analysis of ordinary least squares models for the monomer melting point clearly showed that such models suffer from over-prediction.
- The models have been used to predict the properties of two cyanate ester systems that have not yet been synthesized, but could easily be produced for future validation experiments.